

Cross-linkable Fumed Silica-Based Composite Electrolytes: Effect of Monomer on Electrochemical and Rheological Properties

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Introduction

Electrolytes for lithium batteries must have acceptable ionic conductivity ($>10^{-3}$ S/cm at 25°C), and be chemically and electrochemically stable. Furthermore, electrolytes should be mechanically strong and easily processable¹. Since these properties are usually mutually exclusive, novel electrolytes are needed to meet these material requirements. Composite polymer electrolytes (CPEs) consisting of low-molecular weight polyethers, lithium salts, and surface-functionalized fumed silica are being developed in our laboratories to produce materials with high conductivity and mechanical stability². The mechanical stability stems from the formation of a three-dimensional network of interacting fumed silica aggregates. The native hydroxyl groups on the fumed silica particles can be partially replaced by other functional groups, such as octyl or methacrylate, to tailor the mechanical strength without affecting the electrochemical properties. To further improve the mechanical strength of the CPEs, the methacrylate groups can be subsequently crosslinked to form a chemical cross-linked CPE rather than a physical cross-linked CPE. A monomer, e.g., butyl methacrylate (BMA), is also added to tether the fumed silica particles together and thus forming a robust solid electrolyte.

The purpose of this work to examine the effect of the monomer on the electrochemical and mechanical properties of cross-linked CPEs. Specifically, we want to investigate how the interactions between the base electrolyte and monomer affect the resulting properties of the CPE.

Experimental

Our work uses dual-functionalized fumed silica obtained from Baker's group at Michigan State University³. These fumed silicas have varying amounts of octyl and methacrylate groups attached to the surface and are denoted as TOM (X:Y) (where X is the moles of methacrylate groups and Y is the moles of octyl groups). The base electrolyte consists of poly(ethylene glycol) dimethyl ether (PEGdm) of varying molecular weight (M_n = 250 or 500), lithium bis(trifluorosulfonyl)imide (lithium imide), and methacrylate monomer, i.e., BMA of varying weight fraction (0-20%). The CPEs are thermally cross-linked at 80°C for 24 hours using 1% 2,2'-azo-bis-isobutyronitrile (AIBN) as the initiator. The resulting CPEs are vacuum-dried at elevated temperatures to remove unreacted monomer.

Results and Discussion

The conductivity as a function of temperature for CPEs before and after crosslinking for three different TOM fumed silicas; TOM 4:1, TOM 1:1, and TOM 4:1 is shown in Figure 1. The results indicate that the surface group has a negligible effect on the conductivity before or after crosslinking⁴. Furthermore, the crosslinking reactions results in only a factor of two reduction in conductivity after crosslinking even as the elastic moduli increases three orders of magnitude (data not shown). This suggests that the crosslinking reaction occurs primarily between adjacent fumed silica particles thereby

unaffected the bulk transport properties of the base electrolyte. This conclusion is further supported by lithium transference number measurements, which indicate that the base electrolyte and crosslinked CPE have similar lithium transference numbers (~ 0.23)⁴. Although these CPEs exhibit good mechanical and electrochemical properties, initial results indicate that the films do not form stable interfaces with lithium metal, as shown in Figure 2. The crosslinked CPE exhibits significantly higher interfacial impedance when compared to the base electrolyte with and without fumed silica⁴.

This work determines the underlying reasons for the poor interfacial stability of the crosslinked CPEs and develops possible avenues for mitigating this poor interfacial stability. For example, the effect of the methacrylate monomer chain length is investigated to determine if the relative solubility of the monomer in the base electrolyte is important. The ionic transport, interfacial stability, and cell-cycling of these CPEs are correlated with the bulk properties of the material components to further optimize the performance of the composites.

References

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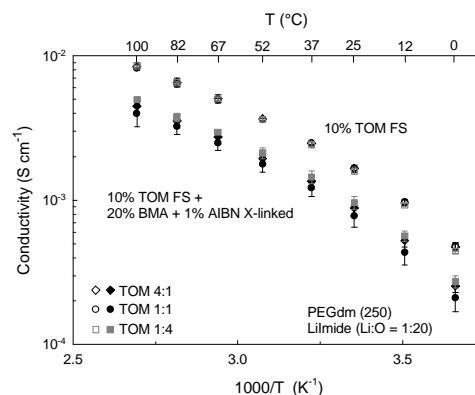


Figure 1. Conductivity of cross-linkable CPEs containing PEGdm(250) and various dual-functionalized fumed silicas (TOM 1:1, TOM 4:1, and TOM 1:4).

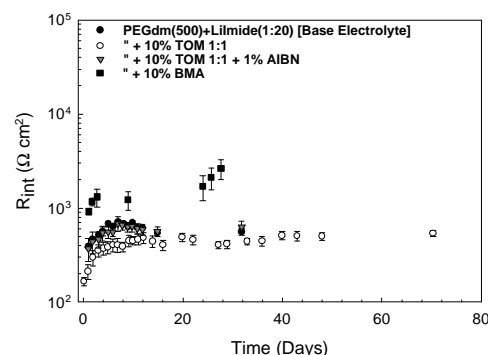


Figure 2. Time-dependent stability of lithium/CPE interface for various uncross-linked CPE compositions.